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METHOD FOR MANUFACTURING POLYPHENYLENE ETHER POWDER WITH  
IMPROVED PARTICLE SIZE DISTRIBUTION  
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## Specification

### 1. Title of the invention

Method for Manufacturing Polyphenylene Ether Powder  
with Improved Particle Size Distribution

### 2. Claims

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1. A method for manufacturing a polyphenylene ether powder with an improved particle size distribution, characterized by the fact that a molded body with a density of 0.7-1.055 g/cm<sup>3</sup> was generated by compression-molding a polyphenylene ether powder at a temperature of 5-200°C; and the molded body obtained is re-pulverized so that the content of fine particles with a particle diameter of 1 μm or smaller is set to 0.5 wt% or less of the entire content.

2. The method for manufacturing a polyphenylene ether powder with an improved particle size distribution of Claim 1, characterized by the fact that the ratio of particles with a particle diameter of 3 μm-5 mm existing in the powder in which the molded body is re-pulverized is 90 wt% or more of the entire content.

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<sup>1</sup> Numbers in the margin indicate pagination in the foreign text.

3. The method for manufacturing a polyphenylene ether powder with an improved particle size distribution of Claim 1, characterized by the fact that fine particles with a particle diameter of 0.5  $\mu\text{m}$  or smaller exist at 0.005 wt% or more in the polyphenylene ether powder before the compression molding.

3. Detailed explanation of the invention

[0001]

(Technical field of the invention)

The present invention pertains to a method for improving a polyphenylene ether powder to a powder with excellent handling characteristic and safety and high extrusion productivity by reducing fine particles in the polyphenylene ether powder.

[0002]

(Prior art)

Techniques for manufacturing a polyphenylene ether by oxidation-polymerizing a phenolic compound are described in Japanese Kokoku Patent No. Sho 45[1970]-23555, Japanese Kokai Patent Application Nos. Sho 64[1989]-33131, Sho 52[1977]-897, etc. In order to recover a polyphenylene ether resin from a polymer solution polymerized by these methods, a method that adds methanol, etc., as base solvents of the polyphenylene ether and recovers a polymer

by precipitating is generally employed. At that time, the polymer particles being precipitated include considerably fine particles. For this reason, the handling characteristic of the powder was poor, the powder was easily flown, and a considerable consideration was also required in terms of safety such as powder dust explosion. Also, when the resin was extruded and granulated, since the powder characteristics were poor, the productivity was dropped by biting inferiority, etc.

[0003] As presented in Japanese Kokoku Patent No. Sho 45[1970]-587, etc., in the method that precipitates such a polymer by contacting a base solvent of a polyphenylene ether resin with a polymer solution containing the polyphenylene ether resin, it has already been known that the conditions for the precipitation of the polymer have a large influence on the polyphenylene ether resin particle diameter. According to this method, the polymer solution was heated up to the vicinity of the boiling point of the solution, and methanol, etc., as base solvents of the polyphenylene ether resin had to be added as fast as possible, the operation was difficult and complicated.

[0004] Also, in Japanese Kokoku Patent No. Sho 55[1980]-17775, a method that thickens the particle diameter of a polyphenylene ether resin powder by a heat treatment in a

water dispersed system of the polyphenylene ether powder containing an organic solvent is presented, however in this method, water with a high specific heat must be used, and the energy cost is raised, causing much disadvantages.

[0005] In Japanese Kokai Patent Application No. Hei 7[1995]-97441, an attempt of improving the flying prevention by adding a surfactant of powder particles and removing a static electricity being generated in the powder is mentioned. In this method, the process was complicated, compared with its effect, so that the economical efficiency was also inferior.

[0006]

(Problems to be solved by the invention)

The reason why the handling characteristic of the polyphenylene ether powder is lowered that fine particles are included and the average particle diameter is small. In other words, particles with good powder handling characteristic are particles that have few fine particles and have an appropriate particle size. Therefore, in order to improve the powder handing characteristic of polyphenylene ether, the reduction of fine particle is required. However, in the above-mentioned presented examples, there are much difficulties in achieving this purpose. The purpose of the present invention is to

improve the handling characteristic of a polyphenylene ether powder by a simpler and efficient method.

[0007]

(Means to solve the problems)

These inventors reviewed the problems in earnest to achieve the above-mentioned purpose. As a result, surprisingly, it was discovered that a molded body with a sufficient strength could be easily obtained by applying a pressure to a polyphenylene ether powder in a certain specific temperature range. Furthermore, it was discovered that if the molded body obtained was re-pulverized, a polyphenylene ether powder with excellent handling characteristic in which fine particles were largely reduced could be obtained. Then, the present invention was completed.

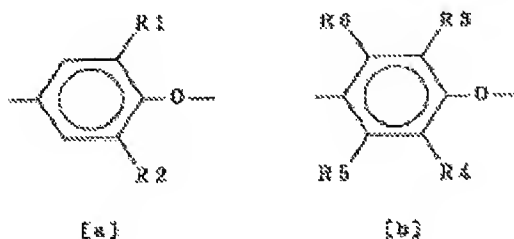
[0008] In other words, the present invention provides a method for manufacturing a polyphenylene ether powder with an improved particle size distribution characterized by the fact that a molded body with a density of  $0.7\text{--}1.055\text{ g/cm}^3$  was generated by compression-molding a polyphenylene ether powder at a temperature of  $5\text{--}200^\circ\text{C}$ ; and the molded body obtained is re-pulverized so that the content of fine particles with a particle diameter of  $1\text{ }\mu\text{m}$  or smaller is set to 0.5 wt% or less of the entire content.

[0009] Next, the present invention is explained in detail.

[0010] As the polyphenylene ether resin being used in the present invention, a homopolymer or copolymer in which the following general formula (1)

[0011]

(Structure 1)



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(In the formula, R1, R2, R3, R4, R5, and R6 represent monovalent residues such as alkyl group having 1-4 carbons, aryl group, halogen, and hydrogen, and R5 and R6 are not simultaneously hydrogen.)

[0012] is a repeated unit and the constitutional unit consists of the above-mentioned (a) and (b) can be used.

As representative examples of the homopolymer of the polyphenylene ether group resin, homopolymers such as poly(2,6-dimethyl-1,4-phenylene) ether, poly(2-methyl-6-ethyl-1,4-phenylene) ether, poly(2,6-diethyl-1,4-phenylene) ether, poly(2-ethyl-6-n-propyl-1,4-phenylene) ether, poly(2,6-di-n-propyl-1,4-phenylene) ether, poly(2-methyl-6-n-butyl-1,4-phenylene) ether, poly(2-ethyl-6-isopropyl-1,4-



phenylene) ether, poly(2-methyl-6-chloroethyl-1,4-phenylene) ether, and poly(2-methyl-6-hydroxyethyl-1,4-phenylene) ether are mentioned.

[0013] The polyphenylene ether copolymer includes polyphenylene ether copolymers mainly constituted by a polyphenylene ether structure such as copolymer of 2,6-dimethylphenol and 2,3,6-trimethylphenol or copolymer of o-cresol or copolymer of 2,3,6-trimethylphenol and o-cresol.

[0014] Also, in the polyphenylene ether group resin of the present invention, other various phenylene ether units, which have been proposed that they may exist in the polyphenylene ether resin, may also be included as a partial structure. As examples of the proposal of the coexistence at a small amount, 2-(dialkylaminomethyl)-6-methylphenylene ether unit, 2-(N-alkyl-N-phenylaminoethyl)-6-methylphenylene ether unit, etc., described in Japanese Kokai Patent Application Nos. Sho 63[1988]-12698 and Sho 63[1988]-301222 are mentioned.

[0015] Also, a structure in which diphenoquinone, etc., are bonded at a small amount in the main chain of polyphenylene ether is included.

[0016] Furthermore, a polyphenylene ether modified with a compound having a carbon-carbon double bond described in Japanese Kokai Patent Application Nos. Hei 2[1990]-276823,

Sho 63[1988]-108059, Sho 59[1984]-59724, etc., for

instance, is also included.

[0017] The molecular weight of the polyphenylene ether resin being used in the present invention is 1,000-100,000 as the number average molecular weight. Its preferable range is 6,000-60,000. The number average molecular weight of the present invention is a number average molecular weight converted into polystyrene attained by using a calibration curve of a standard polystyrene according to a gel permeation chromatography.

[0018] The influence of the particle size distribution of the polyphenylene ether resin as a raw material on the particle size distribution of the powder obtained by the method of the present invention is small. For this reason, when the raw material powder includes a larger amount of fine particles, the improvement effect of the powder handling characteristic is large. The particles with a particle diameter of 0.5  $\mu\text{m}$  or smaller being included in the raw material powder are preferably 0.005 wt% or more of the entire content. More preferably, if the content of the particles with a particle diameter of 0.5  $\mu\text{m}$  or smaller in the raw material powder is 0.03 wt% or more, the powder handling characteristic can be considerably improved.

[0019] Also, as a molding machine being employed in the present invention, for example, a compression molding machine such as compressive roll type, briquetting roll type, and tableting molding machine. If the pressurization can be carried out until the density becomes  $0.7\text{--}1.055\text{ g/cm}^3$  in a temperature range of  $5\text{--}200^\circ\text{C}$ , the effects of the present invention can be sufficiently obtained.

[0020] Also, as a pulverizer being employed in the present invention, coarse crusher, intermediate pulverizer, and fine pulverizer are mentioned. As examples of the coarse crusher, jaw crusher, gyratory crusher, shredder, etc., are mentioned. As examples of the intermediate pulverizer, impact pulverizer such as hammer mill and disintegrator, roll pulverizer, edge runner, etc., are mentioned. As example of the fine pulverizer, centrifugal pulverizer, ball mill, vibratory mill, colloidal mill, mortar, hand mill, etc., are mentioned.

[0021] In the conventional methods, only the compression-molded body with a low strength could be obtained and could not withstand practical uses, however a molded body with a sufficient strength could be obtained by the present invention. As a result, with the addition of a pulverizing process after molding, a polyphenylene ether powder with a

particle size distribution in which fine particles were largely reduced and the handling was easy could be obtained.

[0022] The temperature range of the powder during the compression molding was required to be 5–200°C. If the temperature is lower than 5°C, a molded body with a sufficient strength cannot be obtained. If the temperature is higher than 200°C, amine being included in the /4 polyphenylene ether is separated, and the quality is lowered during the working. More preferably, if the temperature range during the compression molding is set to 80–165°C, a stronger molded body with excellent quality can be obtained.

[0023] In the present invention, it is necessary for the density of the molded body to be in a range of 0.7–1.055 g/cm<sup>3</sup>. If the density of the molded body is lower than 0.7 g/cm<sup>3</sup>, a sufficient strength cannot be rendered to the molded body, and when the molded body is re-pulverized, a large amount of fine particles is generated. If the compression is carried out at a molded body density of higher than 1.055 g/cm<sup>3</sup>, a local heat is generated by the shear during the molding, the molded body is melted, so that an enormous energy is required for re-pulverization and a large amount of fine particles is generated. Also, the amine being included in the polyphenylene ether is

separated by the shear heat, and the quality is lowered during the working. More preferably, if the density is set to 0.75-1.04 g/cm<sup>3</sup>, the molded body does not receive a local shear heat and can be drawn out as a cohered body of a strong powder with few melted parts. With the re-pulverization of the molded body, a powder with good powder characteristics can be obtained.

[0024] The re-pulverization can be applied by using the above-mentioned machine, and the content of the fine particles with a particle diameter of 1 μm or smaller can be reduced to 0.5 wt% or less of the entire content by re-pulverizing. Then, it is preferable for the ratio of the particles of 3 μ-5 mm to simultaneously set to 90 wt% or more of the entire content.

[0025]

(Embodiment of the invention)

Next, the present invention is explained in detail by application examples, however the present invention is not limited at all to these examples.

[0026]

Application Examples 1-4

As a raw material of this test, a poly (2,6-dimethyl-1,4-phenylene) ether (hereinafter, called PPE) powder with a bulk density of 0.527, an intrinsic viscosity (in

chloroform at 30°C) of 0.53, a particle content of 60 wt% having a particle diameter of 100  $\mu\text{m}$  or smaller, a particle content of 12 wt% having a particle diameter of 10  $\mu\text{m}$  or smaller, and a particle content of 0.09 wt% having a particle diameter of 0.5  $\mu\text{m}$  or smaller was used. As a molding machine, a roller compacter having rolls with a diameter of 258 mm and a width of 38 mm was employed. The roller compacter had two rolls, and the PPE powder was pushed into between the rolls by a screw installed at a supply part, and compressed by the roll parts, so that a plate-shaped molded body was obtained. Also, a hammer mill type pulverizer was employed in the pulverization. The particle diameter in the pulverizer was adjusted by a screw attached to the hammer mill so that a powder with a diameter of 5 mm or smaller was discharged.

[0027] Using the roller compacter, the following moldings were carried out.

- (1) Temperature: 120°C, molded body density: 0.795 g/cm<sup>2</sup>  
(molding pressure: 30 kg/cm<sup>2</sup>)
- (2) Temperature: 120°C, molded body density: 0.820 g/cm<sup>2</sup>  
(molding pressure: 40 kg/cm<sup>2</sup>)
- (3) Temperature: 120°C, molded body density: 0.845 g/cm<sup>2</sup>  
(molding pressure: 50 kg/cm<sup>2</sup>)

(4) Temperature: 120°C, molded body density: 0.895 g/cm<sup>2</sup>  
(molding pressure: 70 kg/cm<sup>2</sup>)

The molded bodies obtained under the molding conditions (1), (2), and (3) were white cohered bodies, and the molded body obtained under the molding condition (4) was a cohered body containing a partially semitransparent melted body. Furthermore, as a result of the pulverization of these molded bodies, the small particle contents of the powder particles obtained were as follows.

[0028]

(Table 1)

	1 μm以下	3 μm以下	10 μm以下	30 μm以下
原料	1.09重量%	2.89重量%	12.4重量%	27.5重量%
(1)	0.05重量%	0.08重量%	0.16重量%	1.21重量%
(2)	0.03重量%	0.05重量%	0.12重量%	0.82重量%
(3)	0.02重量%	0.04重量%	0.11重量%	0.22重量%
(4)	0.01重量%	0.02重量%	0.04重量%	0.06重量%

1. 1 μm or smaller
2. 3 μm or smaller
3. 10 μm or smaller
4. 30 μm or smaller
5. Raw material
6. wt%

[0029]

Application Example 5

Similarly to Application Examples 1-4 except for setting the molding condition to (5) temperature: 160°C, molded body density: 1.031 g/cm<sup>2</sup> (molding pressure: 160 kg/cm<sup>2</sup>) and employing briquette rolls having recessions with a diameter of 5 mm in the roll parts as a molding machine, an operation was carried out. The molded body obtained was a partially semitransparent melted body. Furthermore, as a result of the pulverization of this molded body by a method similar to that of Application Examples 1-4, the small particle contents of the powder particles obtained were as follows.

[0030]

(Table 2)

	1 μm以下	3 μm以下	10 μm以下	30 μm以下
原料	1.0重量%	2.6重量%	12.4重量%	27.5重量%
(5)	0.0重量%	0.0重量%	0.02重量%	0.0重量%

1. 1 μm or smaller
2. 3 μm or smaller
3. 10 μm or smaller
4. 30 μm or smaller
5. Raw material
6. wt%

[0031]

Comparative Examples 1 and 2



Similarly to Application Examples 1-4 except for setting the molding conditions to (6) temperature: 120°C, molded body density: 0.650 g/cm<sup>2</sup> (molding pressure: 5 kg/cm<sup>2</sup>) and (7) temperature: 160°C, molded body density: 0.685 g/cm<sup>2</sup> (molding pressure: 5 kg/cm<sup>2</sup>), an operation /5 was carried out. The molded bodies obtained under the molding conditions were white cohered bodies. In these molded bodies, folds were generated, and the molded bodies were easily cracked even by the hand. Furthermore, as a result of the pulverization of these molded bodies by a method similar to that of Application Examples 1-4, the small particle contents of the powder particles obtained were as follows.

[0032]

(Table 3)

	1 μm以下	3 μm以下	10 μm以下	30 μm以下
原料	1.08重量%	2.69重量%	12.4重量%	27.5重量%
(6)	0.87重量%	1.98重量%	8.71重量%	25.4重量%
(7)	0.54重量%	1.79重量%	8.24重量%	21.7重量%

1. 1 μm or smaller
2. 3 μm or smaller
3. 10 μm or smaller
4. 30 μm or smaller
5. Raw material
6. wt%

[0033] If the molded body density is  $0.7 \text{ g/cm}^3$  or smaller, a molded body with a sufficient strength cannot be obtained.

As a result, small particles of  $10 \text{ }\mu\text{m}$  or smaller are generated by pulverizing, and the improvement effect of the powder handling characteristic is small.

[0034]

Comparative Examples 3 and 4

Similarly to Application Examples 1-4 except for setting the molding conditions to (8) temperature:  $3^\circ\text{C}$ , molded body density:  $0.605 \text{ g/cm}^2$  (molding pressure:  $70 \text{ kg/cm}^2$ ) and (9) temperature:  $3^\circ\text{C}$  (molding pressure:  $4 \text{ kg/cm}^2$ ), an operation was carried out. The molded body obtained under the molding condition (8) was a white cohered body. In this molded body, folds were generated, and the molded body was easily collapsed even by the hand. Under the molding condition (9), the generation of a molded body with a density of about  $0.550 \text{ g/cm}^3$  was attempted, however if the molding pressure was lowered, the raw material powder was slipped between the rolls, so that a molded body with an intended density could not be obtained.

Furthermore, as a result of the pulverization of the molded body obtained under the molding condition (8) by a method similar to that of Application Examples 1-4, the small particle contents of the powder particles obtained were as follows.

[0035]

(Table 4)

	1 $\mu\text{m}$ 以下	3 $\mu\text{m}$ 以下	10 $\mu\text{m}$ 以下	30 $\mu\text{m}$ 以下
原料	1.59重量%	2.69重量%	12.4重量%	27.5重量%
(8)	0.98重量%	2.44重量%	11.1重量%	27.3重量%

1. 1  $\mu\text{m}$  or smaller
2. 3  $\mu\text{m}$  or smaller
3. 10  $\mu\text{m}$  or smaller
4. 30  $\mu\text{m}$  or smaller
5. Raw material
6. wt%

[0036] If the molding temperature is set to 5°C or lower, the density of the molded body is not raised, and a molded body with a sufficient strength cannot be obtained. If the generation of a molded body with a low density is attempted, even a molded body cannot be obtained in some cases. Even if the molded body is obtained, small particles of 10  $\mu\text{m}$  or smaller are generated by pulverizing and returned to a powder without a big difference from the raw material.

[0037]

#### Comparative Example 5

Similarly to Application Examples 1-4 except for setting the molding condition to (10) temperature: 170°C, molded body density: 1.059 g/cm<sup>2</sup> (molding pressure: 420 kg/cm<sup>2</sup>), an operation was carried out. The molded body discharged from the rolls was a tea brown melted body, and if this molded body was cooled after molding, a very strong bulk was formed. Furthermore, this molded body was pulverized by a method similar to that of Application Examples 1-4, however many non-pulverized bulks remained on a screen of the pulverizer. The non-pulverized bulks remaining on the screen was 33.4 wt% to the pulverizer feed.

[0038]

(Effects of the invention)

As mentioned above, according to the method of the present invention, fine particles could be considerably reduced from a polyphenylene ether resin powder, so that the resin powder can be simply improved to a powder with excellent powder characteristics, easy handling characteristic, and high extrusion productivity.

